Steroidal Sapogenins*

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XII. Survey of Plants for Steroidal Sapogenins and Other Constituents

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This is a report of the chemical examination of the second 1,000 samples received in a survey of plants for steroidal sapogenins. Data are given for 997 samples, representing 598 identified species, 201 unidentified lots, 392 genera, and 129 families. There is no previously published chemical information on about 60 per cent of the species examined. Quantitative data are given for the occurrence of 11 steroidal sapogenins. These were found almost exclusively in *Yucca, Agave,* and *Dioscorea.* A new sapogenin, named markogenin, was found in *Y. schidigera.* Qualitative data are given for the occurrence of the following groups of constituents: flavonols, alkaloids, tannins, and unsaturated sterols.

PAPER NUMBER VII in this series covered the survey of the first 1,000 samples (1). The present report is a continuation of it and covers the second 1,000 samples. The objective and assay procedures were described in detail in the former report and are not repeated here.

The data include the kinds and amounts of steroidal sapogenins found, and qualitative tests for saponins, flavonols, alkaloids, tannins, and unsaturated sterols. There are 997 samples, representing 598 identified species, 201 unidentified lots, 392 genera, and 129 families. There is no published chemical information on about 60 per cent of the species examined.

PROCUREMENT

The material represents a general sampling of the plant kingdom, as evidenced by the 364 genera in 107 families not included in the first thousand. Besides this continued general survey of the plant kingdom, an extensive collection was made of species in the genera *Dioscorea* and *Agave*.

Collections of *Agave* were obtained primarily by H. S. Gentry in Mexico and the southwestern United States and from the living collection maintained at the Huntington Botanical Garden in San Marino, Calif. He also collected numerous samples of *Dioscorea* in Mexico.

General collections were obtained not only from the above-mentioned areas but also from several cooperators in the southeastern United States, Brazil, Colombia, Okinawa, and elsewhere. Approximately half the collections, however, were procured from permanent stock maintained at the Division of Plant Exploration and Introduction gardens at Coconut Grove, Fla.; Glenndale, Md.; and Chico, Calif.

RESULTS

A table has been prepared giving the data for each sample—its origin and identification, results of the hemolysis tests, kinds and amounts of steroidal sapogenins found, and qualitative findings for flavonols, alkaloids, tannins, and sterols. Because of space limitations, this table cannot be given here. It has, however, been prepared in processed form as AIC-367 and may be obtained on request from the U. S. Department of Agriculture, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

In Table I the steroid data are rearranged to show their occurrence by species.

A positive hemolysis test for saponin was obtained in about 50% of the species. Steroidal sapogenins were found, however, almost exclusively in *Agave, Yucca,* and *Dioscorea,* the exceptions being *Manfreda* (Amaryllidaceae) and *Cordyline* (Liliaceae).

Four rarer steroidal sapogenins—kammogenin, samogenin, yammogenin, and yuccagenin—found in the first series were not found in the present one. However, a hitherto unknown one was found in the by-product leaf powder from the production of fiber from *Yucca schidigera* (sample 1686-0). It was named markogenin (2), spirostan-2ξ,3β-diol, a 2,3-dihydroxy analog of sarsasapogenin.

As stated in the previous report, the nature of the sapogenins found in plants is largely species specific. *Agave* species for the most part produce compounds with a *trans* ring A/B and with *iso* ring configuration at carbon 22. Depending on a number of environmental factors, tigogenin, hecogenin, manogenin, gitogenin, and occasionally chlorogenin are found singly or in combination. In this genus,

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TABLE I.—OCCURRENCE OF THE VARIOUS SAPOGENINS BY SPECIES

Species	No. of Samples	Genin Content, —M. F. B., %— Min.	Max.
Chlorogenin			
Agave brandegeei	1	..	Trace
Agave schidigera	1	..	Trace
Agave sp.	1	..	0.1
Manfreda sp.	1	..	0.5
Yucca angustissima	1	..	Trace
9-Dehydrohecogenin			
Agave aurea	1	..	0.05
Agave cerulata	2	..	Trace
Agave nelsonii	5	Trace	0.2
9-Dehydromanogenin			
Agave aurea	1	..	Trace
Agave cerulata	2	Trace	0.5
Agave goldmaniana	1	..	Trace
Agave nelsonii	5	Trace	0.5
Agave promontorii	1	..	Trace
Agave vexans	1	..	Trace
Agave virginica	1	..	0.1
Diosgenin			
Dioscorea bartlettii	1	..	Trace
Dioscorea composita	1	..	3.8
Dioscorea glauca	1	..	0.2
Dioscorea villosa	5	0.5	1.2
Dioscorea sp.	3	1.0	2.0
Gitogenin			
Agave cerulata	1	..	Trace
Agave goldmaniana	1	..	Trace
Agave roseana	2	..	Trace
Agave schidigera	1	..	Trace
Agave aff. *schidigera*	1	..	0.3
Agave toumeyana	1	..	Trace
Agave virginica	1	..	0.8
Agave sp.	2	Trace	0.2
Manfreda sp.	2	0.7	1.0
Yucca peninsularis	2	Trace	0.3
Yucca whipplei	2	Trace	0.1
Hecogenin			
Agave atrovirens	1	..	0.8
Agave aurea	3	0.1	0.7
Agave brandegeei	3	0.1	0.6
Agave cerulata	3	Trace	0.2
Agave chrysantha	1	..	0.2
Agave datylio	1	..	0.5
Agave deserti	1	..	0.4
Agave expansa	1	..	0.1
Agave goldmaniana	1	..	0.1
Agave nelsonii	5	0.1	0.7
Agave parryi	1	..	0.2
Agave promontorii	2	0.2	0.7
Agave roseana	3	0.1	0.3
Agave shawii	1	..	0.2
Agave sullivanii	1	..	0.1
Agave toumeyana	1	..	0.6
Agave vexans	1	..	0.2
Agave sp.	3	0.2	0.4
Yucca peninsularis	1	..	0.1
Manogenin			
Agave aurea	1	..	Trace
Agave cerulata	2	..	Trace
Agave chrysantha	1	..	Trace
Agave goldmaniana	2	..	Trace
Agave nelsonii	4	Trace	0.7
Agave promontorii	1	..	Trace
Agave roseana	2	..	Trace
Agave shawii	1	..	0.3
Agave toumeyana	1	..	0.3
Agave vexans	1	..	0.2
Agave virginica	1	..	0.2
Agave sp.	2	..	Trace
Markogenin			
Yucca schidigera	1	..	0.2
Sarsasapogenin			
Cordyline neocaledonica	1	..	0.5
Dioscorea bartlettii	1	..	Trace
Yucca angustissima	1	..	0.2
Yucca arizonica	1	..	0.3
Yucca baccata	2	0.5	0.8
Yucca elata	2	0.5	1.3
Yucca faxoniana	1	..	0.2
Yucca schidigera	1	..	2.9
Yucca sp.	2	0.8	0.9
Smilagenin			
Agave carchariodonta	1	..	0.4
Agave difformis	1	..	0.4
Agave goldmaniana	1	..	0.3
Agave lophantha	1	..	1.0
Agave sp.	1	..	1.0
Yucca sp.	1	..	1.5
Tigogenin			
Agave asperrima	1	..	0.4
Agave brandegeei	3	0.1	0.3
Agave cerulata	2	..	Trace
Agave nelsonii	1	..	0.1
Agave promontorii	1	..	0.1
Agave roseana	4	0.1	0.6
Agave schidigera	1	..	0.1
Agave aff. *schidigera*	1	..	0.7
Agave sullivani	1	..	Trace
Agave sp.	4	Trace	1.6
Manfreda sp.	1	..	0.6
Yucca faxoniana	1	..	0.3
Yucca peninsularis	3	0.4	0.9
Yucca whipplei	2	0.3	0.6

hecogenin is probably found most frequently, although rarely alone. A few agaves produce smilagenin with the *cis* ring A/B and *iso* carbon 22 configuration. In these cases, the sapogenin is usually not accompanied by isomeric or modified forms. Sarsasapogenin with a *cis* ring A/B and normal carbon 22 configuration was again found as the sole or predominant constituent of a number of western yuccas. However, coastal yuccas, both from the Southwest and Southeast, produce tigogenin and gitogenin. As stated in the previous paper, *Dioscorea* species produce diosgenin as the sole or predominant steroid.

The evidence presented in this and the preceding report, with few exceptions, permits the following generalization. Sapogenin configuration at carbon 5 and carbon 22 is genus and species specific and cannot be altered by the plant or by environmental conditions. Ketonic and hydroxyl groups, however, can be added or removed by numerous species, resulting in the formation of mixtures of sapogenins.

None of the first 1,000 samples gave a triple test for flavonols. In the present list, however, three were found—leaves of *Diervilla richesse* and *Lonicera* sp. in the Caprifoliaceae and leaves and fruit of *Garcinia spicata* in the Hypericaceae. Krewson *et al.* (4), point out that of 27 species of *Eucalyptus*

examined for rutin, only two contained it. We obtained a test for flavonol in *E. staigeriana* (Myrtaceae), not one of the species hitherto examined. It remains to determine whether this flavonol is rutin.

No test for alkaloid was obtained in 141 samples of *Dioscorea* tubers—18 identified species and 85 lots of unidentified—native to North, Central, and South America, and to the West Indies. In 42 samples native to the rest of the world, alkaloids were found in seven species. This, together with other published evidence, has led to the generalization that the alkaloids probably do not occur in *Dioscorea* in the Western Hemisphere but that they do occur in some Old World species (3). No sapogenins were found in *Dioscorea*-containing alkaloids. Of the species which gave a two- or three-plus test for alkaloids, the following are the first on record: *Lycoris squamigera* (Amaryllidaceae); *Buxus harlandi* (Buxaceae); *Lophocereus schottii* (Cactaceae); *Dioscorea dumetorum* (Dioscoreaceae); *Adenocarpus foliosus, Cassia brasieliensis, C. emarginata, C. excelsa, Peltogyne nitens, Pithecellobium flexicaula* (Leguminosae); *Neillia longiracemosa* (Rosaceae); *Cephalotaxus henryi* (Taxaceae).

As to tannins, the samples for most families are too few for generalization. However, tannins appear to occur frequently in Anacardiaceae, Caprifoliaceae, Ericaceae, Leguminosae, Myrtaceae, and Rosaceae.

As in the first series, unsaturated sterols were generally abundant and frequent.

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